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The influence of static pre-stretching on the mechanical ageing of filled silicone rubbers for dielectric elastomer applications

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Keywords: pre-stretching, mechanical ageing, silicone composite, PDMS, dielectric elastomer

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ABSTRACT

Dielectric elastomer (DE) pre-stretching is a key aspect of attaining better actuation performance, as it helps prevent electromechanical instability (EMI) and usually lowers the Young's modulus, thus leading to easier deformation. The pre-stretched DE is not only susceptible to a high risk of tearing and the formation of mechanical defects, but films with sustained and substantial strain may also experience mechanical degradation. In this study a long-term mechanical reliability study of DE is performed. Young's moduli, dielectric breakdown strengths and dielectric permittivities of commercial silica-reinforced silicone elastomers, with and without an additional 35% (35 phr) of titanium dioxide (TiO₂), were investigated after being subjected to pre-stretching for various timespans at pre-stretches to strains of 60 and 120%, respectively. The study shows that mechanical stability when pre-stretching is difficult to achieve with highly filled elastomers. However, despite the negative outlook for metal oxide-filled silicone elastomers, the study paves the way for reliable dielectric elastomers by indicating that simply post-curing silicone elastomers before use may increase reliability.

1.0 INTRODUCTION

The reliability of dielectric elastomer (DE) transducers depends on the types of material used, as well as fabrication techniques and design and transducer operating conditions (such as maximum stretching, applied frequency and amplitude of the applied voltage). The acrylic double-adhesive VHB 4910, produced by 3M, is one of the best-performing elastomers with respect to actuation strain (s) at a given applied field, and it chiefly outperforms silicone-based elastomers over short time scales. Silicone elastomers, however, possess a faster actuation response as well as reliability over time, since performance remains more or less unaltered up to about 10 million cycles when pre-stretching is avoided. [1] Pre-stretching is well-known to be a prerequisite for the actuation of acrylic-based elastomers, since it simultaneously reduces thickness, decreases the Young's modulus and suppresses electro-mechanical instability (EMI). [2–4] The effect of the first two parameters can be seen from the equation of actuation derived by Pelrine et al. [3]:

$$s = -\epsilon_r \epsilon_0 \frac{(V/d)^2}{Y} \quad \text{Eq. 1}$$

where s is actuation strain, V is applied voltage, d is the thickness of the film and Y is the Young's modulus.

Pre-stretching has also been shown to cause the alignment of elastomer chains in the plane of stretching. [5] This alignment, which is perpendicular to the direction of the electric field, leads to an increase in breakdown strength, because charge carrier movement is impeded. [6] For acrylics, pre-stretching is also favourable due to strain-softening, whereas for silicone elastomers the elastomer usually does not show the same tendency and in many cases strain-hardening behaviour actually sets in. However, pre-stretching remains very favourable for silicone elastomers, as largely improved actuation strains can be obtained through the avoidance of EMI.

The most common failure modes of DE transducers are pull-in instability, dielectrical breakdown and material strength failure [7, 8]. Electromechanical pull-in instability, also known as electromechanical instability (EMI), was identified by Stark and Garton [9] and occurs when

Maxwell pressure locally exceeds the compressive stress of the elastomer [4, 10]. For silicone elastomers, mechanical strength failure is very seldom a failure mode, due to the ultimate extensibility of silicone elastomers usually exceeding 300%. Common actuation strains introduced in silicone elastomers are of the order of 20%, so even with pre-stretching the overall strain is far below their maximum extensibility. For silicone elastomers to make the very most of their potential, i.e. approach actuation strains of the order of their maximum extensibility, greater energy – and thus permittivity – is required.

The major disadvantage of silicone elastomers over acrylics is their low dielectric permittivity. Several approaches have been developed to enhance dielectric permittivity, with the addition of metal oxides being the most frequently investigated due the ease of elastomer formulation. TiO₂-silicone composites have by far been the most commonly investigated elastomer system due to the availability of nanosized TiO₂ particles with various surface functionalizations. More complex approaches exist such as the covalent grafting of dipoles [11–13] and the creation of heterogeneous elastomers with hard and soft domains from controlled network formation [14–17]. Incorporating rigid fillers, such as titanium dioxide, into the cross-linked PDMS matrix increases the dielectric permittivity of the resulting composite elastomer. Mechanical properties are also affected, with results varying according to particle size and surface treatment, from reinforcing to softening [18–22]. On the other hand, a thinly filled elastic film that maintains high strain for a given period of time will, to some extent, suffer mechanical ageing at the microscopic level. The Payne and Mullins effects explain hysteresis in the mechanical properties of filled elastomers. The Payne effect refers to the effect of the strain dependence of the dynamic viscoelastic properties of filled elastomers above their glass transition temperature [23]. Clement et al. [24] investigated the Payne effect in SiO₂-filled PDMS elastomers, and they posited it as the existence of a gradient in elastomeric chain mobility from the PDMS filler interface to the bulk, leading to a stress-softening effect at low strains upon “initial activation” of the elastomer. Clement et al. [25] also investigated the Mullins effect, i.e. the stress-softening phenomenon that occurs in elastomers during the first deformation of a given strain [26]. They attributed Mullins softening to bond ruptures or elastomer chain slippage (as illustrated in Figure 1). Additionally, they observed the dependency of the Mullins effect on the degree of filler dispersion. They found

that non-homogeneity in the spatial distribution of SiO_2 inside the elastomer matrix exhibits a greater Mullins effect due to the fact that larger local strains were acquired in regions with high concentrations of SiO_2 . Due to its disruptive nature, stress softening has often been considered as damaging, but it does not necessarily lead to failure [27]; in general, it just leads to strain-history-dependent mechanical properties, though this dependency can be avoided by stretching the elastomer to more than its maximum actuation strain before applying it in products. Irradiation ageing has previously been studied by Stevenson et al. [28], but during such experiments crosslinking density changed, whereas in this study crosslink density remains constant.

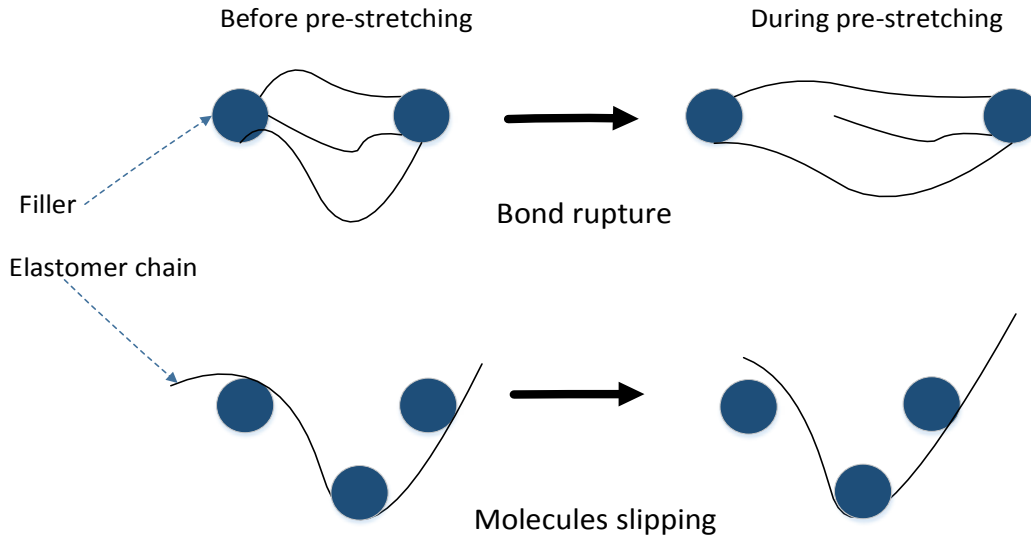


Figure 1: Physical explanations of the Mullins effect.

Generally, silicone elastomers are commercially synthesised through the equilibration polymerisation of cyclic oligomers and end groups in the presence of acid or basic catalysts [29]. One of the disadvantages of this process is the production of by-products as a result of the reaction, consisting of unreacted cyclic oligomers [30]. These residues are mobile within the silicone, and they can also migrate to a device interface. This migration during post-manufacture changes the elastomer surface as well as its mechanical properties such as tensile strength, tear strength, maximum elongation, etc. [31]. As reported by Brook et al. [32], these volatile siloxanes from commercial silicones usually remain within the elastomer when post-curing has

been omitted. Post-curing is usually conducted by heating the elastomer far above its curing temperature but below its degradation temperature for some time. Brook et al. [32] showed that the mechanical properties of the elastomer were enhanced (a larger Young's modulus, greater tensile strength and lower maximum extensibility) upon post-curing. In this case, post-curing was performed by heating a cured elastomer at 200°C for 4 hours subsequent to the traditional curing procedure, where the most common conditions for dielectric silicone elastomers are curing at ~120°C for 10-30 minutes. [33] To our knowledge the effect of post-curing on, for example, dielectric breakdown strength has never been investigated, since the fraction of volatiles is so low (usually cited at 1-2% by the elastomer supplier) that it seems irrelevant.

In order to introduce reliable DE-based products, the pre-stretching frame should be designed in such a way as to impart uniform pre-stretching to the elastomer film over a large area, regardless of whether it is a symmetrical or non-symmetrical pre-stretch [7]. There is a high risk of tearing at the corners of the grips used to hold the thin polymeric film in the pre-stretch equipment, which would lead to premature material strength failure, as the thin films are prone to tearing [7]. With respect to the elastomers, precautions are also required. Micro-voids, deviations in film thickness, surface roughness, inhomogeneous mechanical stiffness, dust particles, contaminants and scratches are the most common defects in thin elastomer films. For acrylics it was shown that during mechanical tests, additional groove-like defects rapidly appear at the film edges attached to rigid supports, and they expand gradually as the test continues [7]. The propagation of such cracks/grooves at stress gradients will age the material faster, thereby leading ultimately to mechanical failure.

As reported by Meunier et al. [34], unfilled PDMS lacks the Mullins effect, hysteresis and strain rate dependency. However, for DE applications filled, reinforced silicones are required to obtain acceptable performance. This study was performed in order to understand the intrinsic mechanical behaviour of pre-stretched PDMS elastomers, with and without additional permittivity enhancing fillers, over time. Furthermore, the study aims at elaborating how mechanical ageing affects other parameters relevant to the DE being used, namely the Young's modulus, electrical breakdown strength and dielectric permittivity.

2.0 METHODOLOGY

2.1 Materials

Four different compositions from two commercial silicone elastomers, without and with one type of permittivity enhancing filler (TiO_2), were investigated. The elastomers were Elastosil[®] LR 3043/30 A/B and ELASTOSIL[®] RT[®] 625 A/B. POWERSIL[®] LR[®] 3043/30 A/B is a high-viscosity LSR and is supplied as a two-part system. The mixing ratio of parts A and B is 1:1. ELASTOSIL[®] RT[®] 625 A/B is an RTV elastomer, which is also supplied as a two-part system. The mixing ratio for parts A and B is 9:1. The solvent OS-20 (an ozone-safe, volatile methylsiloxane (VMS) fluid) was obtained from Dow Corning and added in order to get consistent viscosity formulation.

The investigated elastomers are of Elastosil[®] LR 3043/30 A/B and ELASTOSIL[®] RT[®] 625 A/B, respectively, and are denoted as LSR and RTV, respectively. The permittivity-enhancing filler added is alumina-silica-zirconia surface-treated hydrophobic rutile titanium dioxide (TiO_2) Sachtleben[®] R420[®] from Sachtleben Chemie, Duisburg, Germany, while the average primary particle size is 250 nm. The filler is added in a weight percentage of the original elastomer (i.e. phr) of 35%. The resulting elastomers are referred to as LSR and RTV composites, respectively. Solvent (OS-20) is also added to both $\text{SiO}_2/\text{TiO}_2$ -filled elastomers, to reduce the viscosity of the formulations and thereby ease the coating of thin films.

2.2 Sample preparation

Thin films were carefully prepared based on the procedures described in Zakaria et al. [35] – as summarised below.

Part B of the elastomer, the solvent and the filler were mixed with a DAC 150FVZ (Hauschild Co., Germany) speed mixer at 3000 rpm. After 5 minutes of mixing, part A of the material was added and mixed for another 5 minutes at 2000 rpm. Glass plates were coated with the premixes

using a thin 3540 bird applicator film (Elcometer, Germany). The samples were cured in an oven for 5 minutes at 75°C and subsequently for 10 minutes at 115°C. The thin films were removed from the glass plates, stored between 50 µm-thick ethylene-tetrafluorethylene (ETFE) foils and then kept in a desiccator until use. For this study, two sample thicknesses were targeted by using different blade gaps, namely 150 µm (relatively thinner films) and 200 µm (relatively thicker films). Film thicknesses were approximately 34-88 µm and 52-119 µm for the thin and thick samples, respectively. Film details can be seen in Table 1.

Table 1: Details of prepared SiO₂-filled (commercial) and SiO₂-TiO₂-filled (composite) PDMS films.

| Sample ID | Material | Thickness | Pre-stretch (%) |
|-----------|------------------|-----------|-----------------|
| A1 | RT625 | Thin | 60 |
| A2 | RT625 | Thin | 120 |
| A3 | RT625 | Thick | 60 |
| A4 | RT625 | Thick | 120 |
| B1 | LR304330 | Thin | 60 |
| B2 | LR304330 | Thin | 120 |
| B3 | LR304330 | Thick | 60 |
| B4 | LR304330 | Thick | 120 |
| C1 | RT625+35%R420 | Thin | 60 |
| C2 | RT625+35%R420 | Thin | 120 |
| C3 | RT625+35%R420 | Thick | 60 |
| C4 | RT625+35%R420 | Thick | 120 |
| D1 | LR304330+35%R420 | Thin | 60 |
| D2 | LR304330+35%R420 | Thin | 120 |
| D3 | LR304330+35%R420 | Thick | 60 |
| D4 | LR304330+35%R420 | Thick | 120 |

2.2.1 Pre-stretching of the samples

The samples were pre-stretched on an in-house-built frame. The designed frame holds and pre-stretches 150 thin films up to $\lambda = 400\%$. The films were 130 mm in width and 350 mm in length. In order to pre-stretch the films successfully, both ends were rolled with metal rods to prevent slippage. Then the metal rods, together with the stretched films, were attached to the frame, as shown in Figure 2. The films were then covered by 50 µm-thick ETFE foils to prevent them from contamination. Finally, they were stored for different timespans: one day, one week, one month and three months, before they were released for further characterisation.



Figure 2: The device used to pre-stretch the thin filled PDMS elastomer films. The pre-strains were adjusted by changing the position of the metal rods.

2.3 Instrumentation

2.3.1 Silver deposition

Silver depositions were performed on a physical vapor deposition (PVD) chamber system for reliable dielectric measurements. The chamber is fitted with a large butterfly valve to control pumping speed, and it is pumped by an oil diffusion pump (ODP) with a liquid nitrogen trap. The lid is lifted off the chamber whenever samples or targets need to be changed, and the lid wall seal is accomplished by the addition of a large ring. The base vacuum is approximately 2×10^{-5} mbar. The chamber is fitted with an evaporation source (for silver), a DC magnetron sputter source and an RF sputter source (for sputtering non-conducting targets). Silver evaporation was performed on the tungsten boat at the bottom of the chamber. According to the instrument calibration this should result in a sputtering rate of about 1.5 nm/s and produce a monolayer thickness of silver about 50-60 nm thick within 30-40 seconds. Thin silver electrodes ensure sufficient conductivity. More details on the process can be found in Benslimane et al. [36]

2.3.2 Dielectric constant measurement

Dielectric relaxation spectroscopy (DRS) was performed on a Novocontrol Alpha-A high-performance frequency analyser (Novocontrol Technologies GmbH & Co. KG, Germany) operating in the frequency range 10^{-1} – 10^6 Hz at 23°C. Samples were sputtered with silver to provide electrodes 25 mm in diameter, before they were tested for permittivity.

2.3.3 Breakdown measurement

Breakdown measurements were performed on an in-house-built device based on international standards (IEC 60243-1 (1998) and IEC 60243-2 (2001)). The initial thicknesses of the films before pre-stretching was determined with a Leica DMLB microscope along with a USB Thorlabs 2.0 digital camera. The thickness of the stretched film (refer to SI) was calculated as $t_1 = \frac{t_0}{\lambda}$, where t_0 is initial thickness and λ is the stretch ratio. The distance between the two spherical electrodes ($\phi=20$ mm) was set according to sample thickness with a micrometer stage and gauge. An indent of less than 3% of sample thickness was added to ensure that the spheres were in contact with the sample. A step-wise increasing voltage was applied (50-100 V/step) at a rate of 0.5-1.0 step/s, and each sample was subjected to 10 breakdown measurements and an average of the values indicated as the breakdown strength of the sample.

The breakdown measurements were also performed on the stretched films, which were pre-stretched based on the procedure described in Zakaria et al. [37] and as shown in Figure 3.

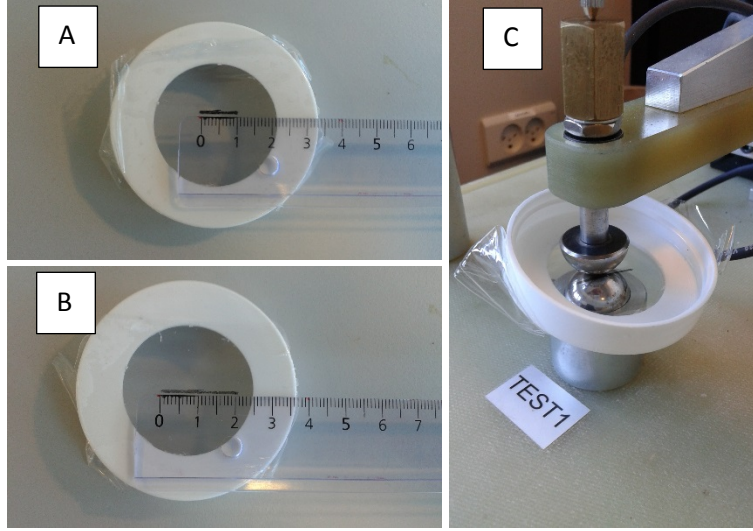


Figure 3: The samples were pre-stretched on a cap with a circular hole. A line was drawn (10 mm) on the unstretched film (a) before the film was extended in the x-direction. (b) The pre-stretched film was slid between 20 mm diameter semi-spherical electrodes (c) for breakdown measurement.

2.3.4 Stress-strain measurement

Uniaxial tensile quasi-static tests were performed to determine Young's moduli at different strains. The quasi-static measurements were carried out on specimens shaped as rectangular strips of about 6 mm x 60 mm in size, by applying a step-wise increasing load and measuring the corresponding elongations from $s=0\%$ to $s=130\%$. Young's moduli were determined from the tangent of the stress-strain curves for strains from 0% to 130%.

3.0 RESULTS AND DISCUSSION

Understanding the effects of static pre-stretching on PDMS films at different timespans is a prerequisite for making reliable DE transducers based on pre-stretched elastomer films. This understanding will be a step toward more reliable products. The natural subsequent step will be understanding the ongoing electrical ageing [38] and electro-mechanical ageing phenomena. However, if the developed elastomer cannot survive a static mechanical ageing test, it is very likely to fail prematurely in a coupled electro-mechanical test. Here we focus on static pre-

stretches of 60 and 120%, respectively, and we also investigate how pre-stretching influences other relevant parameters in relation to DE performance. Since the film thickness of silicone elastomers has been shown to influence strongly electrical breakdown strengths [37] and mechanical properties [39], two thicknesses for each film were investigated, i.e. each elastomer formulation was tested in four configurations at each timespan (thick or thin/60% or 120% pre-stretch), while for the breakdown strength measurements another two configurations were utilised (either non-stretched or stretched to the utilized pre-stretch during the measurement).

3.1 Mechanical ageing

All silicone elastomers tested within this study show a strain-softening effect for strains up to a certain amount (around 60-70%) where after the elastomers strain-harden with increased strains. This characteristic feature leads to a local minimum in the Young's modulus as a function of strain. Figure 4(A) shows the Young's modulus ($Y = \frac{\partial \sigma}{\partial s}$) as a function of strain for samples subjected to pre-stretching for various timespans. The results shown are for thin samples pre-stretched to 120%, as they were shown to be the most susceptible to mechanical ageing. Data for thin films to 60% pre-stretch, as well as thick samples to both 60% and 120%, are shown in the SI. In order to ease the comparison of data, normalisation was performed in Figure 4(b). The normalised Young's modulus $Y_n(s) = \frac{Y(s)}{Y_0(s)}$, where $Y(s)$ = Young's modulus for aged samples at the given strain, and Y_0 is the Young's modulus for the non-aged reference samples at the same strain for the various filled PDMS films at $s = 0$ to 130%.

For commercial elastomers, RTV (A2) and LSR (B2), i.e. pure commercial elastomers, mechanical ageing is not at first glance significant. However, from the normalised diagrams (Figure 4(B)) it is obvious that the dynamics have changed to some extent over time. Initially, it was deemed odd that ageing did not seem to be monotonic. From the results of Brook et al. [32] this discrepancy can be explained by the fact that cyclic silicones from the commercial silicone elastomer remain within the elastomer, as no harsh post-curing has been performed on our elastomers. For the investigated elastomers, mass losses upon heating up to ~250°C have been

investigated previously by using TGA and were of the order of 1-2%.[40] Therefore, upon pre-stretching, the first process taking place –as expected – is Mullins softening, due to the particulate network being broken down. Then, subsequently, after the surface has been partly broken, the cyclic silicones and residual solvent diffuse out of the elastomer, thus leading to hardening of the elastomers [32]. For both commercial elastomers, the diffusion phenomenon seems to be strongest for the ~1 week timescale, whereas for the composite RTV (C2) elastomer, the effect seems to be delayed significantly, and for the composite LSR (D2), the effect is faster and vanishes between one and three months. For the composite LSR, the elastomer shows such a strong Mullins effect that it never regains its original strength after the first (destructive) 130% strain cycle.

The phenomenon of volatile siloxanes diffusing from the PDMS elastomer can be seen clearly on the RTV (A3) and LSR (B3) commercial elastomer samples, as the mechanical properties of the aged films are higher than the reference after pre-stretching from one day up to three months (refer to Figure 2 in SI). Meanwhile, for the composites RTV (C3) and LSR (D3), a lesser effect can be seen, as the elastomers show a rather strong Mullins effect (refer to Figure 2 in SI). Also, when comparing thicknesses, it is evident that the mechanical ageing effect is highly thickness-dependent, since the enhancement of mechanical properties (before the degradation) is significantly slower for thick films.

After the cyclic silicones and residual solvent have evaporated, the commercial RTV elastomer (A) does not demonstrate major changes in mechanical properties. However, the commercial LSR changes its high-strain properties and becomes significantly less strain-hardening over timespans ranging from one to three 3 months. Strain-hardening behaviour is favourable in the context of avoiding electro-mechanical instability (EMI), so it clearly represents a worsening of mechanical properties.

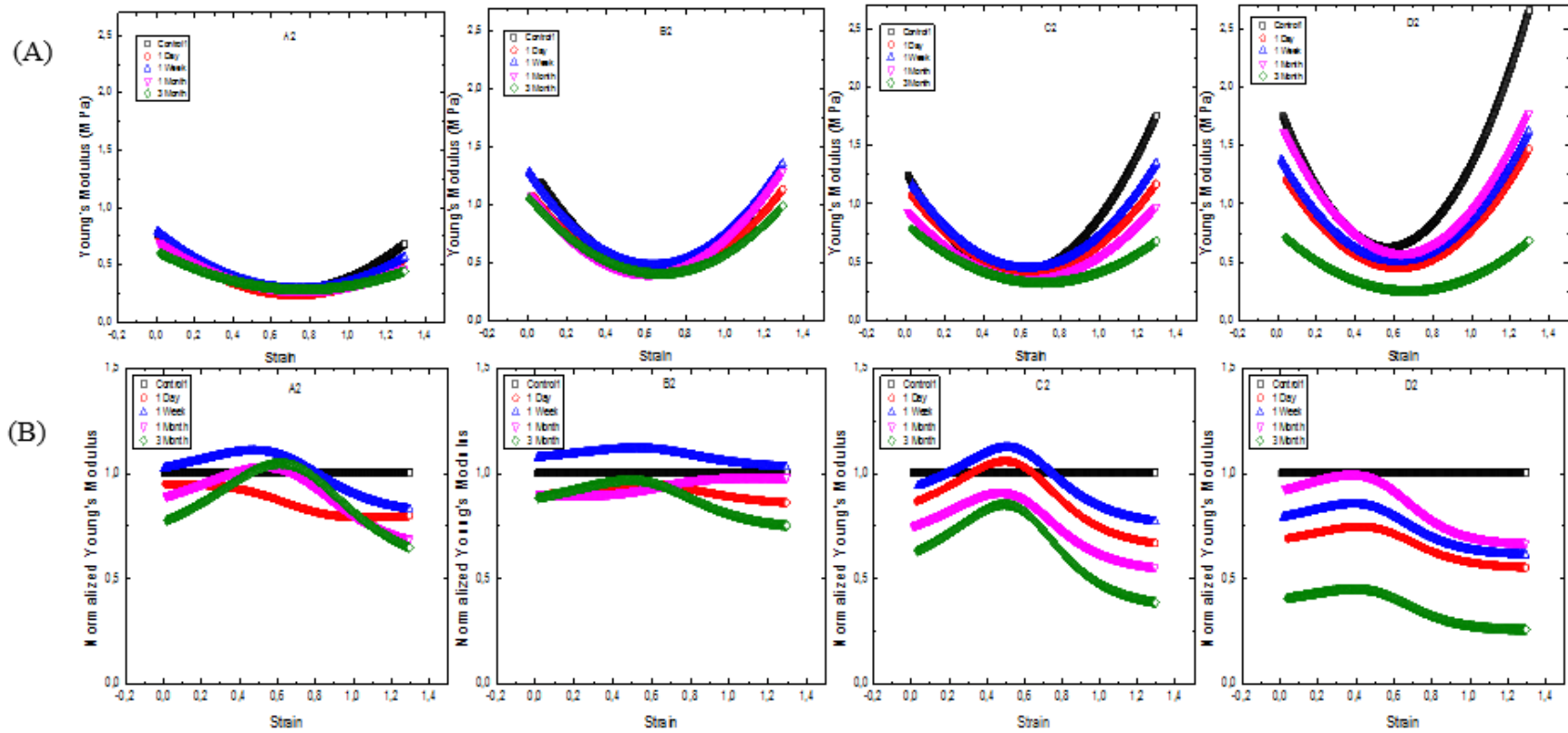


Figure 4: Young's moduli (a) and normalised Young's moduli (b) for investigated elastomers as a function of the strains. (A2) and (C2) are commercial and composite RT625 films, respectively, whereas (B2) and (D2) are commercial and composite LR3043/30 films, respectively. Films were pre-stretched at different timespans (black square: control, red circle: 1 day, blue upwards triangle: 1 week, violet downwards triangle: 1 month and diamond green: 3 months). All elastomeric samples had similar conditions; i.e. thin films (coated with 150 μm blade) and $\lambda= 120\%$ except for the control samples ($\lambda= 0\%$).

Data on the Young's moduli have been condensed in Figure 5, in which the Young's moduli at $s=120\%$ have been plotted as functions of time for both thin and thick films. The most significant observable mechanical degradation was obtained for composite D2, as the Young's modulus at $s=120\%$ of the non-aged reference sample declines by a factor of approximately four after three months of pre-stretching (2.55 MPa and down to 0.66 MPa). However, only slight changes to the Young's moduli at $s=120\%$ were obtained for A2 samples (0.70-0.45 MPa). This indicates a longer term of mechanical reliability for SiO_2 -filled elastomers compared to composite elastomers. This is also expected, as commercial elastomers are formulated to high standards. As reported by Dorfmann and Ogden [41], the effect of stress softening is only present to a small extent in unfilled compounds and elastomers with low filler content.

It is clear that the Young's moduli for different PDMS materials and conditions at $s=120\%$ vary significantly over time. The effect of pre-stretching on the mechanical degradation of filled PDMS films can be seen clearly in Figure 5. The samples that had larger pre-stretches ($\lambda=120\%$) reveal severe mechanical ageing (red circle and violet downward triangle) compared to the samples that were subjected to smaller pre-stretching ($\lambda=60\%$) (black square and blue upward triangle), due to stress-softening increasing progressively in line with the increasing strain. [42] Even though the dependency of mechanical ageing on thickness was not clearly noticeable in Figure 5, nevertheless the coupling of the thin film and a larger strain demonstrates the most severe effect on the mechanical ageing of filled PDMS films. Thick samples will experience delayed ageing, because the constructive evaporation of cyclic silicones and destructive structure changes appear simultaneously at the timescales investigated within this study.

For the two composite formulations, the composite RTV (C2) shows the severest loss of tension on the one month time scale, but it continues to lose tension over time. The composite LSR formulation obviously loses significant tension, with a drop in Young's moduli greater than 50% for all strains investigated following three months of ageing at a pre-stretch of 120%.

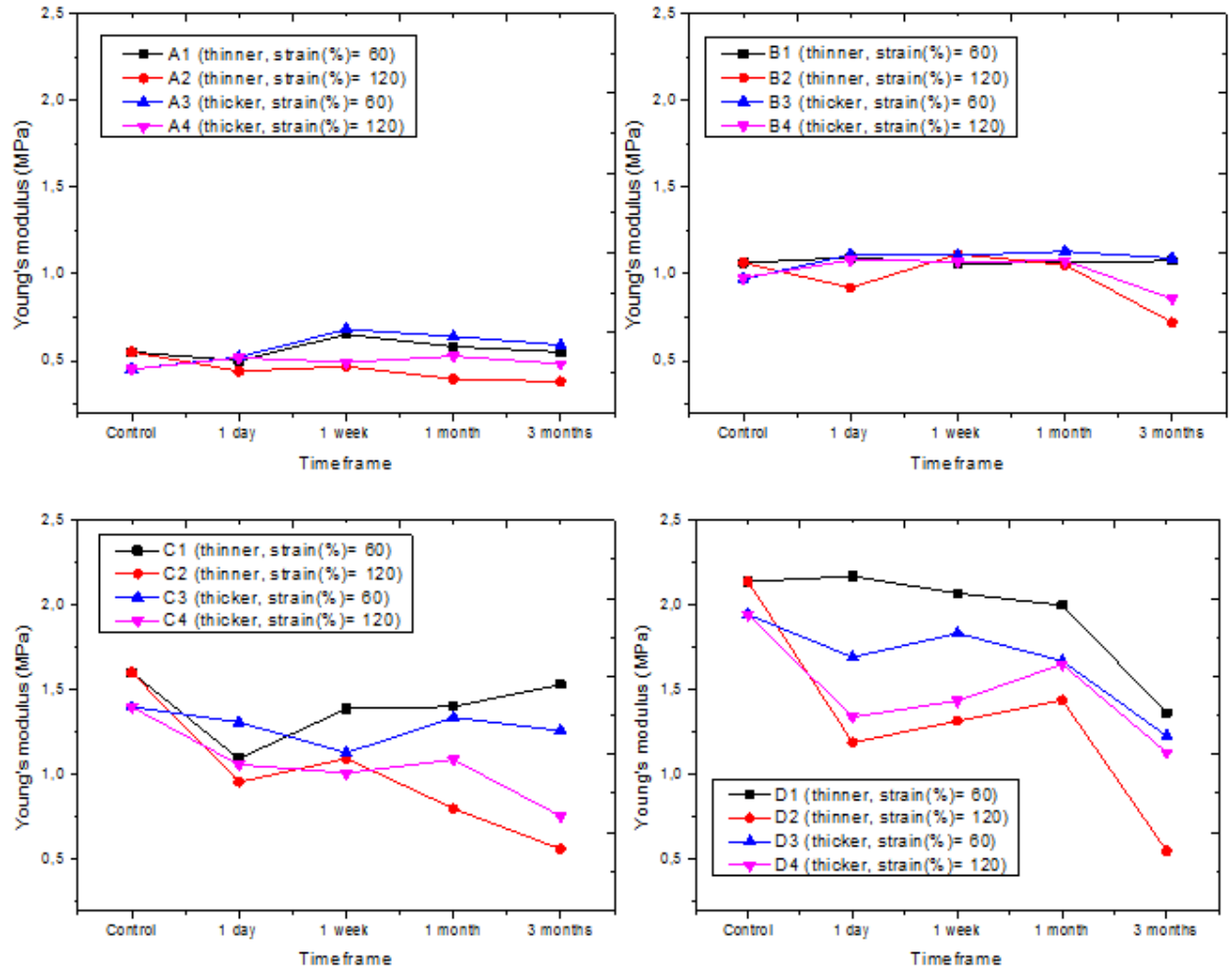


Figure 5: Young's moduli of different samples measured at $s = 120\%$ after pre-stretching from time=0–control to 3 months. A= RT625, B= RT625+35% TiO_2 , C= LR3043/30 and D= LR3043/30+35% TiO_2 . Conditions for A1, B1, C1 and D1= the films were coated with a $150\ \mu\text{m}$ blade (thin films) and $\lambda = 60\%$, A2, B2, C2 and D2= the films were coated with a $150\ \mu\text{m}$ blade (thin films) and $\lambda = 120\%$, A3, B3, C3 and D3= the films were coated with a $200\ \mu\text{m}$ blade (thick films) and $\lambda = 60\%$ and A4, B4, C4 and D4= the films were coated with a $200\ \mu\text{m}$ blade (thick films) and $\lambda = 120\%$.

To illustrate the loss of tension in the elastomers over time, stress-strain diagrams under cyclic loading conditions are shown in Figure 6. The cyclic deformation diagrams are shown for two representative samples (lowest (A) and highest (D) total filler content, respectively). Initially before ageing, the control sample strongly exhibits Mullins softening, as the area of hysteresis loop for the first deformation is approximately three times that of the second deformation for both

the A2 and D2 samples. After constant pre-stretching, the Mullins effect becomes less pronounced for the aged sample, since the area of the initial hysteresis loop decreases significantly.

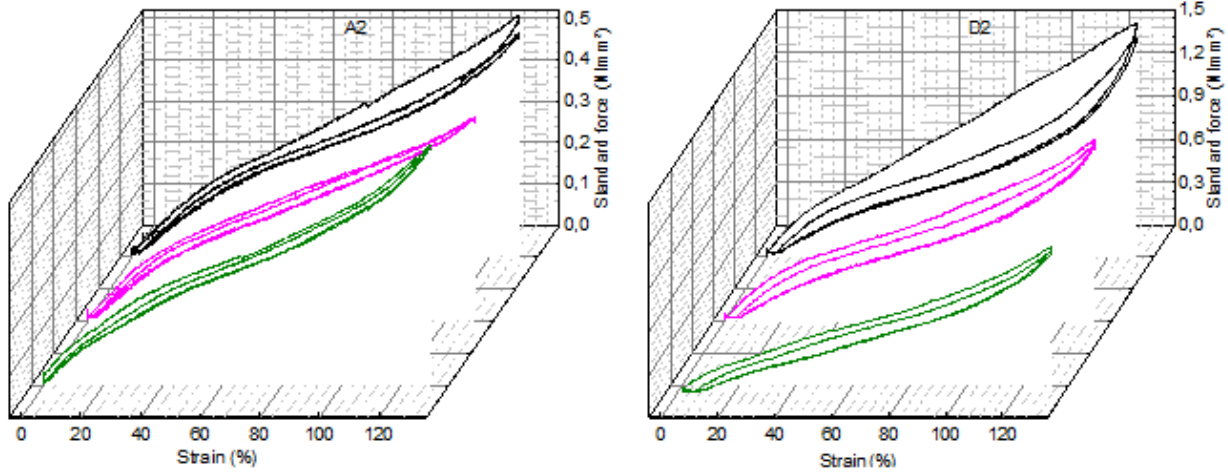


Figure 6: Stress-strain diagrams of control (black), 1 month (violet) and 3 months (green) of RTV elastomer (A2) and composite LSR (D2) sample (pre-stretching 120%).

3.2 Breakdown strength

Since the mechanical properties of pre-stretched PDMS films change over time, it can be argued that the breakdown strengths of filled PDMS films are also likely to change. Figure 7 shows the normalised breakdown strengths ($BD_n = \frac{BD}{BD_0}$, where BD = breakdown strength for aged samples and BD_0 = breakdown strength for non-aged reference samples) for different filled PDMS films and ageing conditions. The results show breakdown strengths for both unstretched and stretched (during breakdown test) PDMS samples. The inconsistency of the results is caused mostly by deviations in sample thicknesses (as can be seen in Table 1 in SI), as breakdown strengths were proved previously to be strongly dependent on the thicknesses of elastomeric films [37], i.e. the thicker PDMS films show low breakdown strength compared to the thin films, due to the increased volume – and thus larger number of defects. The thicknesses of the investigated films cannot be controlled precisely due to different PDMS formulation viscosities, and the variation in thicknesses can be seen in Table 1 in SI. Simultaneously, as mechanical properties change,

breakdown strengths will also change [43], and as discussed previously the Young's moduli do not change monotonically. This behaviour is also observed within the determinations of breakdown strengths. The commercial elastomer RTV shows – for all samples – a maximum in breakdown strength, which is consistent with the maximum in Y . For the LSR, breakdown strength is enhanced at the end of the ageing study, but at present it remains unclear as to why the mechanical data do not support this behaviour. For the composites there is no clear trend except that, overall, breakdown strength decreases after three months of pre-stretching.

For better comparison –without complications aligned with thickness variations – the breakdown strengths of several samples with minimal thicknesses deviations ($\pm 3 \mu\text{m}$) in relation to the control samples were compared, as shown in Table 2. The breakdown results for the one- and three-month samples were chosen, as they show greatest effect of volatile siloxanes diffusion, as shown in SI. The standard deviations were considerably greater for several samples, due to the non-uniformity of film thicknesses and defects contained in the prepared samples, while the major uncertainty of the breakdown data may also indicate bimodal distributions of breakdown strengths for several samples (see Figure 4 in SI). Nonetheless, the data in Table 2 confirm that the breakdown strengths lower in line with mechanical ageing, due to the decrease in the Young's modulus of the aged samples [43].

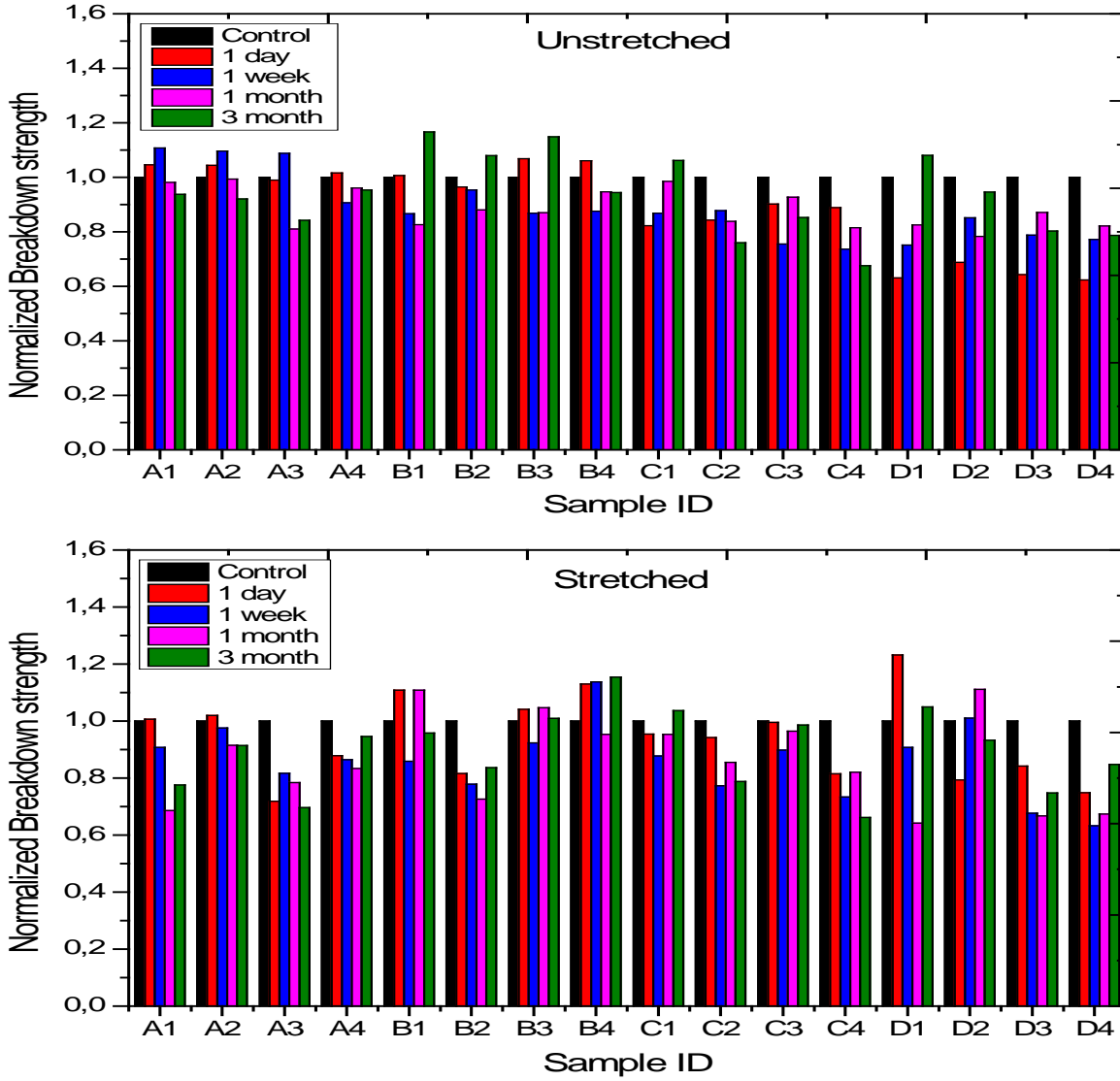


Figure 7: Normalised breakdown strength of unstretched and stretched PDMS films at different timespans. The films were pre-stretched, while breakdown measurements were performed for the stretched samples. A= RT625, B= RT625+35% TiO₂, C= LR3043-30 and D= LR3043-30+35% TiO₂. Conditions for A1, B1, C1 and D1= the films were coated with a 150 μ m blade (thin films) and λ = 60%, A2, B2, C2 and D2= the films were coated with a 150 μ m blade (thin films) and λ = 120%, A3, B3, C3 and D3= the films were coated with a 200 μ m blade (thick films) and λ = 60% and A4, B4, C4 and D4= the films were coated with a 200 μ m blade (thick films) and λ = 120%.

Table 2: Breakdown strengths of several samples that have thickness differences at $\pm 3 \mu\text{m}$ in relation to the thicknesses of the control films

| Sample ID | Control | | | 1 Month | | | 3 Month | | |
|-----------|------------------------------------|---|---|------------------------------------|---|---|------------------------------------|---|---|
| | Sample thickness (μm) | Breakdown strength ($\text{V}/\mu\text{m}$) (Unstretched) | Breakdown strength ($\text{V}/\mu\text{m}$) (stretched) | Sample thickness (μm) | Breakdown strength ($\text{V}/\mu\text{m}$) (Unstretched) | Breakdown strength ($\text{V}/\mu\text{m}$) (stretched) | Sample thickness (μm) | Breakdown strength ($\text{V}/\mu\text{m}$) (Unstretched) | Breakdown strength ($\text{V}/\mu\text{m}$) (stretched) |
| A3 | 106 | 98 \pm 4 | 160 \pm 3 | 108 | 90 \pm 8 | 125 \pm 6 | | | |
| B4 | 63 | 101 \pm 5 | 169 \pm 3 | 66 | 95 \pm 6 | 161 \pm 3 | | | |
| C1 | 67 | 113 \pm 3 | 159 \pm 7 | 67 | 111 \pm 4 | 151 \pm 3 | | | |
| C2 | 67 | 113 \pm 3 | 194 \pm 5 | 64 | 97 \pm 3 | 166 \pm 5 | | | |
| A2 | 73 | 97 \pm 4 | 160 \pm 2 | | | | 76 | 89 \pm 4 | 146 \pm 3 |
| C3 | 89 | 114 \pm 5 | 144 \pm 4 | | | | 88 | 98 \pm 8 | 142 \pm 5 |
| C4 | 89 | 114 \pm 5 | 190 \pm 2 | | | | 88 | 77 \pm 5 | 126 \pm 4 |
| D2 | 41 | 141 \pm 4 | 266 \pm 6 | | | | 41 | 133 \pm 6 | 249 \pm 6 |

3.3 Dielectric properties

When the elastomer changes both the mechanical properties and electrical breakdown strength, it is very likely that the dielectric properties will also change over time. Figure 8 shows normalised storage permittivity ($\epsilon'_n = \frac{\epsilon'}{\epsilon'_0}$, where ϵ' = storage permittivity for aged samples and ϵ'_0 = storage permittivity for non-aged reference samples) for filled PDMS films at a frequency of 10^{-1} and 10^6 Hz, respectively. Despite the unfavourable effect of mechanical ageing on breakdown strength, the dielectric constants of the filled PDMS films improve at both low and high frequencies (10^{-1} Hz and 10^6 Hz) after pre-stretching at given timespans where all aged samples show higher storage permittivity in comparison to the control. This is a clear indication of the complex network structure within the composites (consisting of polymeric network as well as polymer-particle and particle-particle interactions) being altered. This is most likely due to a decrease in particle-particle interactions, i.e. the agglomerates are broken and facilitating smaller particles – and thus increased permittivity. However, the data is so scattered that temperature scans would have been required to perform any general conclusion. The dielectric loss factor does, however, reveal differences in phenomena occurring for the pure elastomers and the composite elastomers. Figure 8 shows the dielectric loss tangent as a function of frequency for samples A2, B2, C2 and D2 at

time=0 and time= 3 months. The results show the dependency of the loss tangent for both composite (C2 and D2) samples in relation to ageing. There is no evidence showing the effect of mechanical ageing on the loss tangent for commercial elastomers (A2 and B2), as there is no significant difference in the permittivities of PDMS and silica. At higher filler loadings, achieving proper dispersion is difficult (despite using a high-speed mixer), and agglomerated particles in the elastomer matrix may occur. Large deformations for a long time interrupt the relatively weak interactions between agglomerated particles (Mullins effect) and thus increase the mobility of the high-permittivity segments in the composite films, as discussed above. Thus, the increase in the loss tangent is assumed to be the result of the mobility of the fillers which separate and thereby increase their effective surface area. This increase can be seen from the loss tangent increasing at low frequencies, due to the predominantly interfacial polarisation.

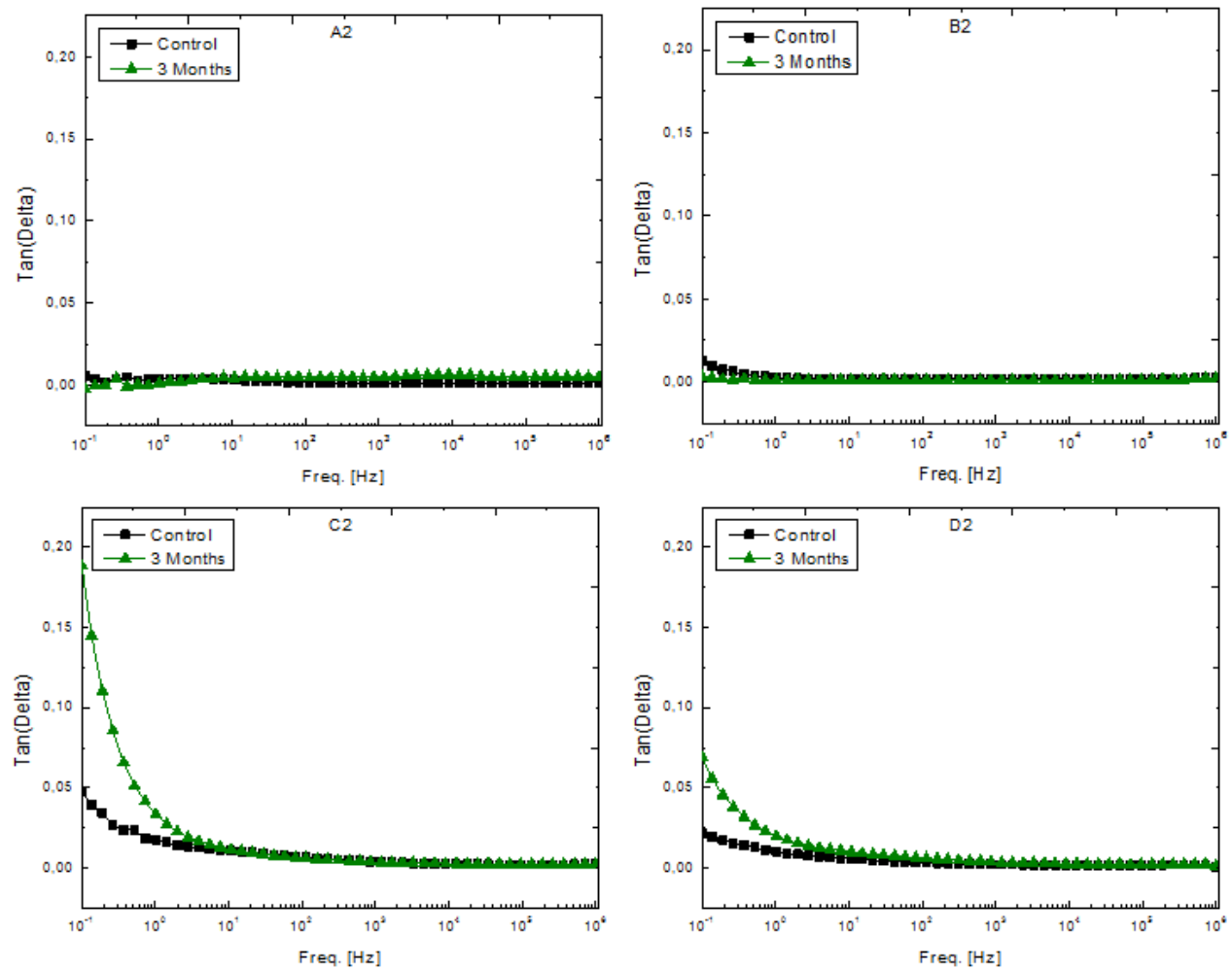


Figure 8: Loss tangents for the A2, B2, C2 and D2 samples after pre-stretching from time=0 to 3 months. (A2) and (C2) are commercial and composite RTV elastomers, respectively, whereas (B2) and (D2) are commercial and composite LSR elastomers, respectively. All elastomeric samples had similar conditions, i.e. thin films and $\lambda=120\%$.

CONCLUSION

Dielectric elastomers with enhanced permittivity are heavily sought after for enhanced actuation, and so many approaches in this respect are being currently developed. The addition of high-permittivity metal oxide fillers to silicone elastomers is a facile method for such an enhancement, but studies so far have focused solely on how the metal oxides affect instant mechanical behaviour. In this study we show that titanium dioxide cannot be added unlimitedly when pre-stretching the elastomer, since the composites lose their tension very quickly. If such high loadings of fillers are required, it is important to further functionalise the particles for better compatibility and integrity. Another important finding is that even commercial silicone elastomers require post-curing for mechanical stability, which is an overlooked feature for silicone elastomers utilised in dielectric elastomers. The two commercial elastomers in this research (RT625 and LR3043/30) both showed improved strength over a time scale of weeks, and thus a decrease in actuation will take place. This phenomenon can be ascribed to the evaporation of volatile cyclic silicones and other residues from elastomers which have had their protective surface broken during pre-stretching. Over a timescale of months, a slight reduction in elasticity takes place due to ageing. In other words, the elastomer will not provide constant actuation over time if it is not ensured beforehand that all volatiles have been removed. The removal of volatiles is additionally favourable, as it increases electrical breakdown strength and thus enhances the reliability of the elastomer.

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